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On an Allylic Type Rearrangement on Treatment of α-Methoxy-2-benzo[b]thienylacetic Acid with Hydrogen Bromide

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Treatment of α-methoxy-3-benzo[b]thienylacetic acid with 30 % hydrogen bromide in acetic acid yielded as expected α-bromo-3-benzo[b]thienylacetic acid, while α-methoxy-2-benzo[b]thienylacetic acid yielded 3-bromo-2-benzo[b]thienylacetic acid. No rearrangement occurred on treating 3- or 2-hydroxymethylbenzo[b]thiophene with the same reagent. The two α-methoxybenzo[b]thienylacetic acids were prepared from the corresponding benzo[b]thienyllithium derivatives through reaction with chloral followed by treatment of the trichloromethyl benzo[b]thienylcarbinols with methanolic potassium hydroxide.

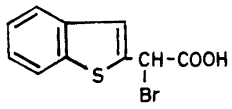
In connection with other work we wished to prepare α-bromo-2-benzo[b]thienylacetic acid (I) and α-bromo-3-benzo[b]thienylacetic acid (II). It was planned to synthesize these compounds in the same fashion as the 3-thienyl analogue, which was prepared in high yield by treatment of α-methoxy-3-thienylacetic acid with 30 % hydrogen bromide in acetic acid at room temperature.[1] The α-methoxy-3-thienylacetic acid was prepared by the reaction of 3-thienyllithium with chloral followed by alkaline rearrangement of trichloromethyl-3-thienylcarbinol in methanol solution.[2]

Attempts to prepare α-bromo-2-thienylacetic acid in the same way from α-methoxy-2-thienylacetic acid were not successful and led only to tar formation.[1]

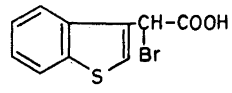
The route used for the methoxy acids in the thiophene series was also feasible in the benzo[b]thiophene case. Halogen-metal interconversion between 3-bromobenzo[b]thiophene[3] and ethyllithium at −70°C yielded 3-benzo[b]thienyllithium, which upon reaction with chloral yielded crude trichloromethyl 3-benzo[b]thienylcarbinol in about 90 % yield. This product was reacted with methanolic potassium hydroxide to yield α-methoxy-3-benzo[b]thienylacetic acid (III) in 12 % yield, based on 3-bromobenzo[b]thiophene.

3-Benzo[b]thiophenecarboxylic acid was prepared in 85 % yield from 3-benzo[b]thienyllithium by reaction with carbon dioxide, and 3-benzo[b]thiophenecarboxaldehyde was prepared in 53 % yield by reaction with *N*-methylformanilide. This is a more convenient route to this compound than the Vilsmeyer formylation of benzo[b]thiophene with *N*-methylformanilide and phosphorus oxychloride, which yields only 9 % of the aldehyde.[4] However, after our work was completed a paper appeared which described the preparation of 3-benzo[b]thiophenecarboxaldehyde in 65 % yield by the reaction of benzo[b]thiophene with dichlorobutyl ether in the presence of titanium tetrachloride (Rieche formylation).[5]

Similar results were recently independently obtained by Dickenson and Iddon, who studied the synthesis and reaction of 3-benzo[b]thienyllithium and who also prepared the aldehyde and acid,[6] among other compounds. The behaviour of 3-bromobenzo[b]thiophene in the halogen-metal interconversion is quite similar to that of 3-bromothiophene, studied extensively by one of the present authors and his coworkers.[7]



I



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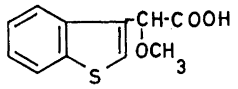
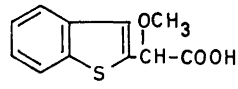
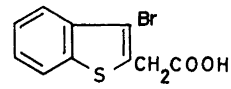


III



IV



V

The reaction of 2-benzo[b]thienyllithium, obtained by direct metalation of benzo[b]thiophene [8] with ethyllithium, with chloral followed by treatment of the intermediate product with methanolic potassium hydroxide yielded α-methoxy-2-benzo[b]thienylacetic acid (IV) in 18 % yield.

When α-methoxy-3-benzo[b]thienylacetic acid was treated with 30 % hydrogen bromide in acetic acid at room temperature the expected α-bromo-3-benzo[b]thienylacetic acid was obtained in quantitative yield. The reaction was complete after about 30 h. The structure was evident from the relative intensities of the aromatic hydrogen and α-CH hydrogen peaks in the NMR spectrum, and also the thiophenic hydrogen resonance could readily be identified.

When α-methoxy-2-benzo[b]thienylacetic acid was treated in the same way with hydrogen bromide in acetic acid 3-bromo-2-benzo[b]thienylacetic acid (V) was obtained. This was evident from its NMR spectrum, which showed absorption for aromatic and aliphatic hydrogens with relative

intensities of four to two and no sharp peak ascribable to a thiophenic hydrogen could be detected. The structure was confirmed by synthesis, starting from 2,3-dibromobenzo[b]thiophene [9] which was converted to 3-bromo-2-benzo[b] thiophenecarboxylic acid by halogen-metal interconversion followed by carbonation. This was in turn converted to methyl 3-bromo-2-benzo[b]thienyl acetate by the Arndt-Eistert synthesis [10] *via* the usual intermediate. The product was identical with the methyl ester obtained from the reaction product from α-methoxy-2-benzo[b]thienylacetic acid and hydrogen bromide.

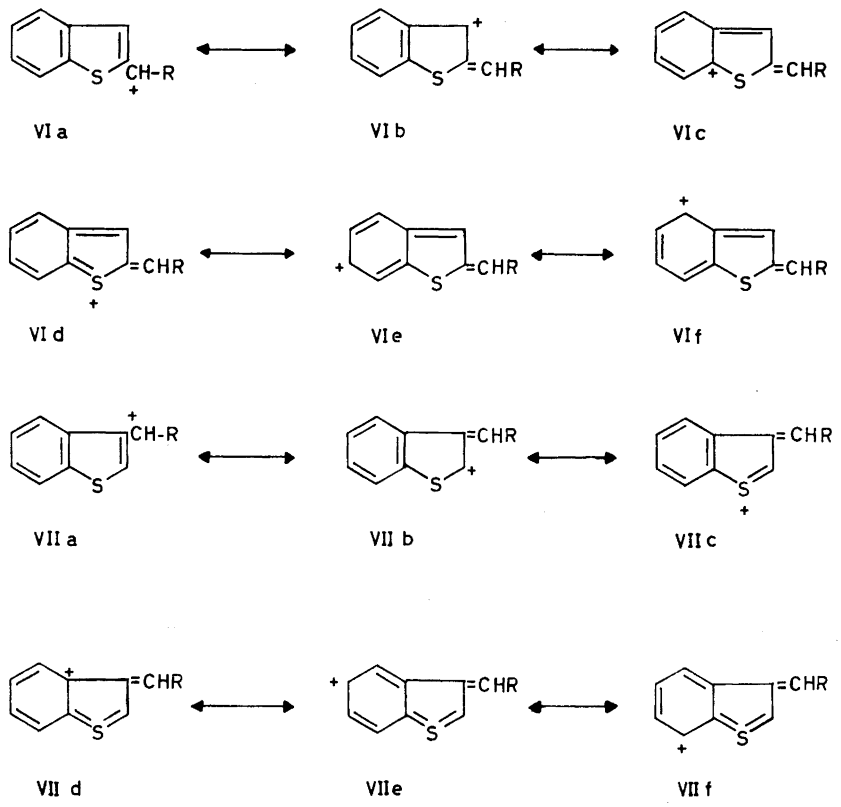
We also found that the carboxyl group was necessary for the rearrangement. Treatment of 2- as well as 3-hydroxymethylbenzo[b]thiophene with hydrogen bromide in acetic acid yielded only the expected bromomethylbenzo[b]thiophenes, as far as could be detected by NMR spectroscopy.

The bromomethylbenzo[b]thiophenes were rather unstable and decomposed within a few days and it was difficult to obtain satisfactory analyses for bromine. The 3-isomer appeared, however, to be somewhat more stable. Both were strong skin-irritants.

With hydrogen chloride in acetic acid the chloromethyl derivative was obtained, and it is thus not necessary to use thionyl chloride in order to transform 2-hydroxymethylbenzo[b]thiophene to the chloromethyl derivative.[11] 2-Hydroxymethylbenzo[b]thiophenes were obtained in good yield by lithium aluminium hydride reduction of the corresponding benzo[b]thiophenecarboxylic acids according to the description of Blicke and Sheets.[11]

Allylic type rearrangements have in a few cases been observed earlier in nucleophilic substitution with heterocyclic substrates. The most well-known case is the reaction of 2-furfuryl chloride with sodium cyanide, which leads to 5-cyano-2-methylfuran and 2-cyanomethylfuran in the proportions 85:15.[12–14] 3-Furfuryl chloride on the other hand yields 2-cyano-3-methylfuran and 3-cyanomethylfuran in the proportions 1:9.[15] The detailed mechanism of this rearrangement seems not to have been studied, but it appears reasonable to assume that the mechanism is similar to the S_N2'-reaction observed for some allylic halides. Due to the strong stabilizing effect of furan and thiophene rings on benzylic type carbonium ions a mechanism *via* such an intermediate cannot be completely excluded. A carbonium ion intermediate has recently been suggested by Campaigne and Neiss [16] to explain the formation of 2 % of 2-cyano-3-methylbenzo[b]thiophene besides 98 % of the expected 3-cyanomethylbenzo[b]thiophene in the reaction of 3-chloromethylbenzo[b]thiophene with sodium cyanide in dimethyl sulphoxide.

The different behaviour of α-methoxy-2-benzo[b]thienylacetic acid compared to 2-hydroxymethylbenzo[b]thiophene may perhaps be understood in the following way. When R=COOH the contribution of resonance structure VIa to the resonance hybride is of lesser importance than when R=H due to the destabilizing effect of the neighbouring carbonyl carbon. It is well known that carbonium ions derived from α-carbonyl compounds are very unstable. The different behaviour of III and IV on treatment with hydrogen bromide is more difficult to rationalize. Formulae VI a-f describe the forms contributing to the structure of the 2-benzo[b]thienylcarbonium ion while VII a-f give the forms contributing to the 3-isomer. We can note that for the 3-isomer it is necessary to place ten electrons around the sulphur (VII d-f) in order to



delocalize the positive charge into the benzene ring. On the other hand for the 3-isomer we have three structures (VII a-c) with the Kekulé resonance of the benzene ring intact, while for the 2-isomer only two (VI a-b) exist.

Thus, considerations of the limiting structures lead to the conclusion that the carboxymethyl carbonium ion (VI, R=CO_2H) can more readily delocalize the positive charge into the benzene ring than the 3-analogue (VII, R=CO_2H). On the other hand, the positive charge on atom 2 should be larger in VII than the positive charge on atom 3 in VI. The latter conclusion is at variance with the experimental results, since it is generally assumed that a resonance stabilized carbonium ion attacks primarily with the atom having the highest positive charge. We have performed some simple HMO calculations on the charge distribution in VI and VII with R=H and CO_2H. The results (Fig. 1) are in good agreement with the more qualitative ones based on the limiting

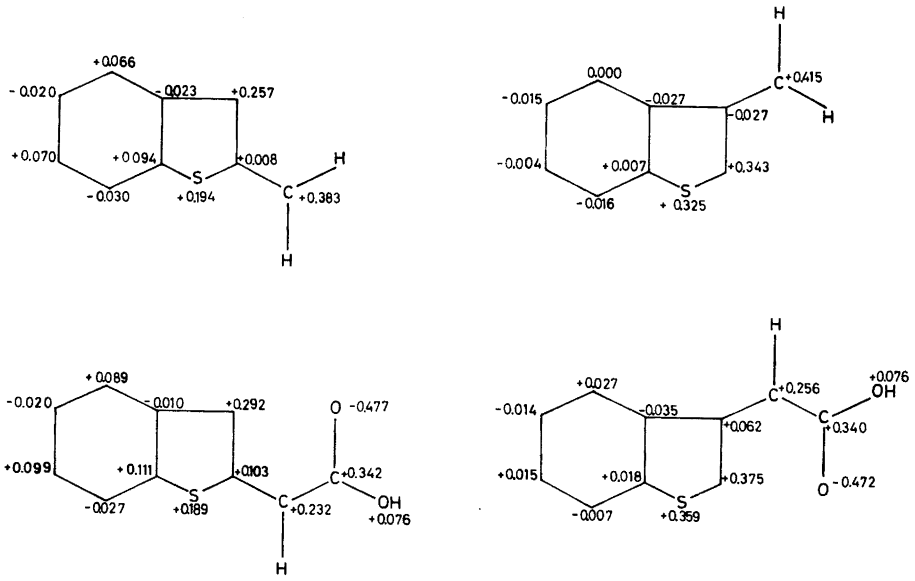


Fig. 1. Charge distributions calculated by the HMO method. ($h_{\ddot{S}} = h_{\dot{O}} = 1.0$, $h_{\ddot{O}} = 2.5$; $k_{C-S} = 0.6$, $k_{C=O} = 1.0$; $k_{C-O} = 0.8$)

structures. The positive charge is much higher on the exocyclic carbon atom when R=H than when R=CO_2H, and the positive charge on atom 2 in VII is much higher than on atom 3 in VI. The expected larger charge delocalization into the benzene ring in VI is also well reproduced. The high positive charge on the sulphur atom in VII and also the high S—C_2 π-bond order (0.623) indicate a relatively high weight for the limiting structure VIIc. The corresponding "sulphonium" structure VId seems to have less weight, since the positive charge on the sulphur atom in VI is much less than in VII, and the S—C_8 bond order is 0.343 in VI. This seems to indicate the importance of the intact Kekulé structure. We have at present no explanation to offer for the lack of agreement between the experimental results and the calculated charge distributions.

It is of course also necessary to check whether product formation is kinetically or thermodynamically controlled.

EXPERIMENTAL

Trichloromethyl-2-benzo[b]thienylcarbinol. To 0.55 mole of ethereal ethyllithium under nitrogen, 67.1 g (0.50 mole) benzo[b]thiophene in 100 ml of anhydrous ether was added dropwise with stirring. The reaction mixture was refluxed for 45 min, cooled and 73.7 g (0.50 mole) of chloral in 100 ml of ether added dropwise. After standing for 15 min the mixture was poured onto ice-water and 10 ml of acetic acid added. The ether phase was separated and the water phase extracted with ether. The combined ether phases were washed with sodium carbonate solution and water, dried over magnesium sulphate,

and the ether evaporated *in vacuo*. 127 g (86 %) of a dark-red oil was obtained. Attempts to purify the oil by distillation at 0.2 mm Hg led to extensive decomposition and only a few grams of crystalline trichloromethyl-2-benzo[b]thienylcarbinol, m.p. 33–34°C, was obtained, so the crude product was used directly in the next step.

α-Methoxy-2-benzo[b]thienylacetic acid. The crude trichloromethyl-2-benzo[b]thienylcarbinol (127 g) was dissolved in 160 ml of methanol. With stirring, 495 ml of 3.7 N methanolic potassium hydroxide was added dropwise at 45°C. The mixture was then refluxed for one hour and allowed to stand overnight and the potassium chloride (70.5 g) filtered off. The solution was evaporated to a small volume and a saturated aqueous sodium chloride solution was added. The precipitated sodium salt was filtered off and washed several times with acetone. 35.5 g sodium salt was obtained which was dissolved in 1 N sodium hydroxide solution with heating. Acidification with 5 N hydrochloric acid precipitated 20.0 g (18 % based on benzo[b]thiophene) of α-methoxy-2-benzo[b]-thienylacetic acid, m.p. 104.5–105.5°C after recrystallisation from benzene. NMR (CD_3COCD_3): $\tau_{COOH} = -0.13$ ppm, $\tau_{benzenic} \approx 2.04-2.75$ ppm, $\tau_{thiophenic} = 2.50$ ppm, $\tau_{CH} = 4.70$ ppm, $\tau_{CH_3} = 6.50$ ppm. [Found: C 58.97; H 4.79; S 14.35. Calc. for $C_{11}H_{10}O_3S$ (222.3): C 59.44; H 4.54; S 14.43].

Trichloromethyl-3-benzo[b]thienylcarbinol. To 0.33 mole of ethereal ethyllithium at −70°C was added under nitrogen and with stirring 65.2 g (0.306 mole) of 3-bromobenzo-[b]thiophene [3] in 100 ml of anhydrous ether. After stirring at −70°C for one hour, 45.0 g (0.306 mole) of chloral in 100 ml of ether was added dropwise. After stirring for 0.5 h, the temperature of the mixture was allowed to rise to 0°C. The same work-up as described for the 2-isomer yielded 78.0 g (91 %) of crude trichloromethyl 3-benzo[b]thienylcarbinol which was used directly in the next step without distillation.

α-Methoxy-3-benzo[b]thienylacetic acid. The crude trichloromethyl 3-benzo[b]thienyl-carbinol was dissolved in 80 ml of methanol, 300 ml of 3.7 N methanolic potassium hydroxide was added dropwise and the mixture refluxed for one hour. The same work-up as described above for the 2-isomer yielded, after adjusting the pH with hydrochloric acid, 8.8 g of the sodium salt, which gave 8.3 g (12 % on 3-bromobenzo[b]thiophene) of α-methoxy-3-benzo[b]thienylacetic acid, m.p. 51–52°C after recrystallisation from benzene. NMR (CD_3COCD_3): $\tau_{thiophenic} = 2.20$ ppm, $\tau_{benzenic} \approx 1.67-2.67$ ppm, $\tau_{CH} = 4.67$ ppm, $\tau_{CH_3} = 6.54$ ppm. [Found: C 59.78; H 4.42; S 14.44. Calc. for $C_{11}H_{10}O_3S$ (222.3): C 59.44; H 4.54; S 14.43].

α-Bromo-3-benzo[b]thienylacetic acid. To a solution of 2.5 g (0.011 mole) of α-methoxy-3-benzo[b]thienylacetic acid in 30 ml of acetic acid was added 26 ml of a 30 % solution of hydrogen bromide in acetic acid. After 30 h the mixture was poured onto ice-water and the precipitate filtered off. 2.6 g (96 %) of α-bromo-3-benzo[b]thienylacetic acid, m.p. 144–145°C, was obtained after recrystallisation from benzene. NMR (CD_3COCD_3): $\tau_{COOH} = 0.00$ ppm, $\tau_{benzenic} \approx 1.75-2.67$ ppm, $\tau_{thiophenic} = 1.97$ ppm, $\tau_{CH} = 3.90$ ppm. [Found: C 44.93; H 2.60; Br 29.78; S 11.89. Calc. for $C_{10}H_7BrO_2S$ (271.8): C 44.30; H 2.60; Br 29.47; S 11.83].

3-Bromo-2-benzo[b]thienylacetic acid. To a solution of 5.0 g (0.022 mole) of α-methoxy-2-benzo[b]thienylacetic acid dissolved in 62 ml of acetic acid was added 50 ml of 30 % hydrogen bromide in acetic acid. The mixture was stirred for 28 h and then poured onto ice-water, which precipitated 5.8 g (98 %) of 3-bromo-2-benzo[b]thienylacetic acid, m.p. 148–151°C, after recrystallisation from ligroin (b.p. 80–120°C). NMR (CD_3COCD_3): $\tau_{COOH} = -0.25$ ppm, $\tau_{benzenic} \approx 2.50$ ppm, $\tau_{CH_3} = 5.95$ ppm. [Found: C 44.44; H 2.97; Br 29.14; S 11.57. Calc. for $C_{10}H_7BrO_2S$ (271.1): C 44.30; H 2.60; Br 29.47; S 11.83].

Methyl 3-bromo-2-benzo[b]thienylacetate. The title compound was prepared in 95 % yield by reaction of 3-bromo-2-benzo[b]thienylacetic acid with ethereal diazomethane. M.p. 48–50°C after recrystallisation from aqueous ethanol. NMR (CD_3COCD_3): $\tau_{benzenic} \approx 2.00-2.67$ ppm, $\tau_{CH_3} = 5.97$ ppm, $\tau_{CH_3} = 6.30$ ppm. [Found: C 46.51; H 3.24; S 11.04; Br 27.58. Calc. for $C_{11}H_9BrSO_2$ (285.2): C 46.33; H 3.18; S 11.25; Br 28.02].

3-Bromo-3-benzo[b]thiophenecarboxylic acid chloride. 12.5 g (0.049 mole) of 3-bromo-2-thianaphthenecarboxylic acid and 32.4 g (0.26 mole) of thionyl chloride were refluxed for 4 h. Most of the thionyl chloride was distilled off, the last residues *in vacuo*. The crystalline product was recrystallized from petroleum ether, yielding 12.5 g (99 %) of 3-bromo-2-benzo[b]thiophenecarboxylic acid chloride, m.p. 140–141°C.

3-Bromo-2-benzo[b]thenoyldiazomethane. To a suspension of 5.5 g (0.020 mole) of 3-bromo-2-benzo[b]thiophenecarboxylic acid chloride was added an ethereal solution

containing 0.060 mole diazomethane. The mixture was stirred for 36 h and the ether removed *in vacuo*, yielding 5.0 g (94 %) of 3-bromo-2-benzo[b]thenoyldiazomethane, m.p. 104–105°C. [Found: C 42.76; H 2.35; S 11.12. Calc. for $C_{10}H_5BrN_2OS$ (281.4): C 42.72; H 1.79; S 11.41].

Methyl-3-bromo-2-thianaphthenylacetate. To a boiling solution of 3.2 g (0.012 mole) of 3-bromo-2-benzo[b]thenoyldiazomethane in 100 ml of methanol was added 4.0 g of silver oxide in portions suspended in 100 ml of methanol. After 4 h charcoal was added, the mixture filtered hot and evaporated. The residue was recrystallized from alcohol yielding 0.5 g (15 %) of methyl-3-bromo-2-benzo[b]thienylacetate, m.p. 48–50°C, after recrystallisation from alcohol having the same IR spectrum as the sample described above.

2-Bromomethylbenzo[b]thiophene. 1.64 g (0.010 mole) of 2-hydroxymethylbenzo[b]-thiophene [11] was dissolved in 60 ml of acetic acid and 26 ml of a 30 % solution of hydrogen bromide in acetic acid was added. The mixture was stirred for 24 h and then poured onto ice and water, which precipitated 2.2 g (96 %) of 2-bromomethylbenzo[b]thiophene, m.p. 61–63°C after recrystallisation from petroleum ether (b.p. 60–80°C). NMR (CD_3OCD_3): $\tau_{benzenic} \approx 2.09-2.84$ ppm, $\tau_{thiophenic} = 2.59$ ppm, $\tau_{CH_2} = 5.09$ ppm. [Found: C 46.8; H 3.03; S 14.1. Calc. for C_9H_7BrS (227.13): C 47.59; H 3.11; S 14.12].

2-Chloromethylbenzo[b]thiophene. To a solution of 1.64 g (0.010 mole) of 2-hydroxy-methylbenzo[b]thiophene in 60 ml of acetic acid was added a solution of 4.2 g hydrogen chloride in 50 ml of acetic acid and the mixture stirred for 24 h. The mixture was then poured onto ice and water to yield 1.4 g (77 %) of 2-chloromethylbenzo[b]thiophene, 55–56°C .NMR (CD_3COCD_3): $\tau_{benzenic} \approx 2.00-2.83$ ppm, $\tau_{thiophenic} = 2.62$ ppm, $\tau_{CH_2} = 5.00$ ppm. Literature value [11] m.p. 55–56°C.

3-Benzo[b]thiophenecarboxylic acid. To an ethereal solution of 0.11 mole of ethyllithium cooled to −70°C was added dropwise under nitrogen with stirring 21.3 g (0.10 mole) of 3-bromobenzo[b]thiophene.[3] After 45 min the mixture was poured onto solid carbon dioxide covered with ether. When the temperature had risen to about −10°C, water and dilute hydrochloric acid were added. The ether phase was extracted with 2 N sodium hydroxide and the combined aqueous layers acidified with dilute hydrochloric acid, precipitating 15.2 g (85 %) of 3-benzo[b]thiophenecarboxylic acid, m.p. 174°C. Literature value [17] m.p. 174–175°C. NMR (CD_3COCD_3): $\tau_{benzenic} \approx 1.84-2.59$ ppm, $\tau_{thiophenic} = 1.37$ ppm.

3-Benzo[b]thiophenecarboxaldehyde. To a solution of 3-benzo[b]thienyllithium prepared as described above from 37.0 g (0.17 mole) of 3-bromobenzo[b]thiophene and 0.20 mole of ethereal butyllithium was added at −70°C 34 g (0.25 mole) of *N*-methylformanilide in 100 ml of anhydrous ether. After 3 hours at room temperature the mixture was poured onto ice and 200 ml of 2.5 N hydrochloric acid. The ether phase was separated and the aqueous layer extracted with ether. The combined ether extracts were washed with dilute hydrochloric acid and sodium bicarbonate solution, dried over magnesium sulphate and the ether removed *in vacuo*. To the residue was added some ethanol and 125 ml of saturated sodium bisulphite solution. After one hour the precipitated bisulphite adduct was filtered off and washed with ether. To a cold aqueous solution of the adduct was added a saturated sodium carbonate solution, which precipitated 14.5 g (53 %) of 3-benzo[b]thiophenecarboxaldehyde, m.p. 56–57°C after recrystallisation from ethanol. Literature value: m.p. 56–57°C,[6] 58°C.[5] NMR (CD_3COCD_3): $\tau_{CHO} = -0.16$ ppm, $\tau_{thiophenic} = 1.34$ ppm, $\tau_{benzenic} \approx 1.84-2.59$ ppm.

3-Bromomethylbenzo[b]thiophene. Treatment of 1.64 g (0.010 mole) of 3-hydroxy-methylbenzo[b]thiophene [11] with hydrogen bromide in acetic acid as described above for the 2-isomer yielded 2.2 g (96 %) of 3-bromomethylbenzo[b]thiophene, m.p 60–62°C after recrystallisation from petroleum ether (b.p. 60–80°C). Although the m.p.'s for the 2- and 3-isomers were similar, they showed differences in their IR spectra. NMR (CD_3COCD_3): $\tau_{benzenic} \approx 1.92-2.67$ ppm, $\tau_{thiophenic} = 2.25$ ppm, $\tau_{CH_2} = 5.10$ ppm. [Found: C 47.0; H 3.74; S 14.1. Calc. for C_9H_7BrS (227.13): C 47.59; H 3.11; S 14.12].

NMR spectra were recorded with a Varian A 60 NMR spectrometer. Mass spectra were obtained on an LKB A–9000 mass spectrometer and IR spectra were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer.

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